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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THERMAL EXPANSION OF HYDROGEN AND CARBON DIOXIDE UNDER CONSTANT PRESSURE.

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The Apparatus.

In a former paper, a new apparatus is described for determining the thermal coefficient of expansion of gases under constant pressure. This yielded preliminary determinations of constancy sufficient to warrant the belief that with greater care as to details the method might give extremely accurate results.* The present paper describes further work with this apparatus, proving that the hope was not a vain one. In this new work it was endeavored not only to avoid all conceivable constant errors, but also to introduce a number of technical improvements. These objects were accomplished by improving the methods for the determination of the constants of temperature, pressure, and of volume, and by making the conditions of the experiments more uniform, thus diminishing the number and magnitude of the corrections to be applied.

Many possible sources of error, due to thermal expansion of standards, were at once eliminated by maintaining the room at a constant temperature. A perfectly firm, immovable foundation for the apparatus was also found necessary, both to guard against the accidental moving of the apparatus and to insure freedom from vibration on the part of the various surfaces of mercury.

A room about six meters square, with walls of masonry and floor of concrete, situated in the basement of Boylston Hall, was therefore chosen. The windows were provided with double layers of glass, and a constant temperature of 200°. C. was maintained by means of a gas stove provided with an automatic electrical gas regulator. The electric regulating current was made and broken by a sealed hydrogen barometer,

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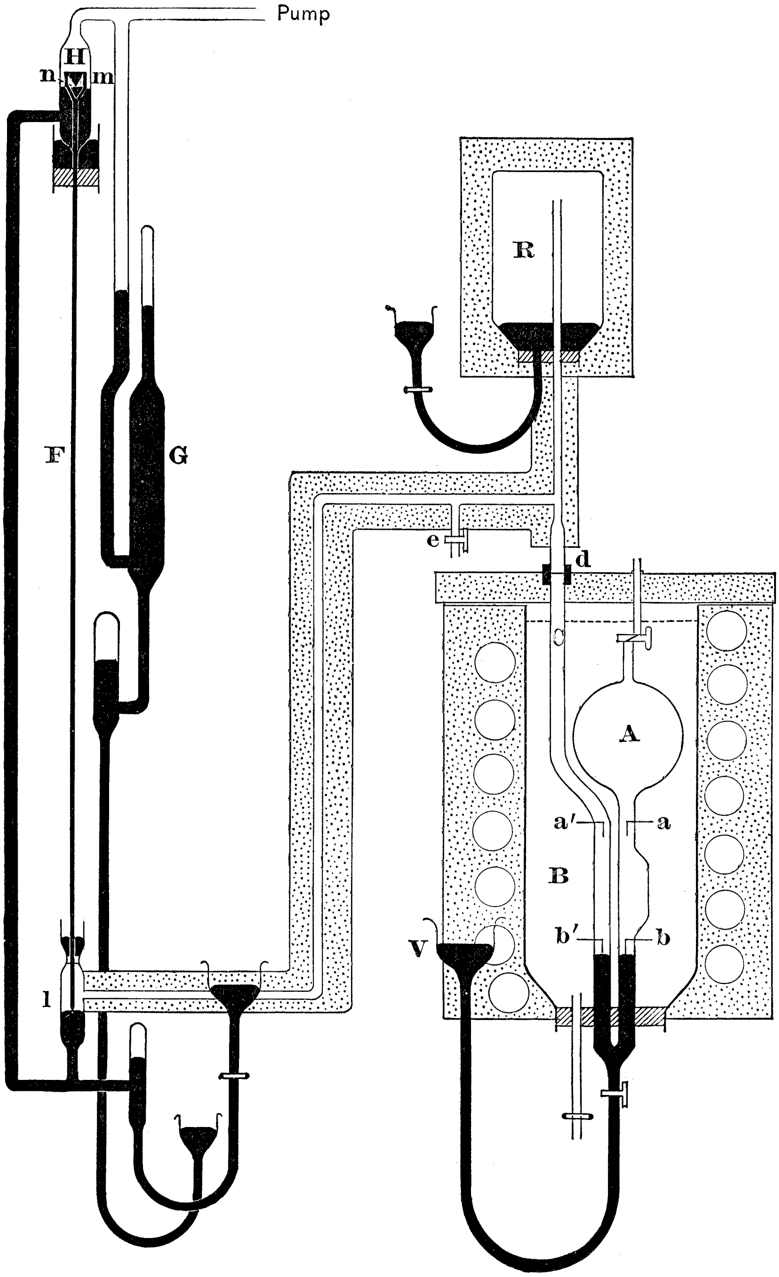
* These Proceedings, **38**, 417 (1902).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provided above with a suitably pointed platinum wire to make the current when the pressure of the warming gas reached a certain point.* An electric fan suspended near the ceiling directed a current of air downward, and thus kept all parts of the room at approximately the same temperature. This arrangement was found to give a temperature constant for hours to the tenth of a degree centigrade and seldom to allow a change of more than a few tenths. The great advantage of a constant-temperature room for this work can scarcely be over-emphasized. Not only are the troublesome corrections for temperature in the pressure readings and the errors due to the unequal expansion of the supports of the apparatus eliminated, but all other errors due to thermal effects, both those foreseen and those possibly overlooked, are also thus diminished, if not made quite improbable.

Here was set up, on very firm supports, the apparatus indicated in the diagram, taken from the previous paper. In this apparatus a definite mass of gas was made to expand between two temperatures under almost constant pressure, the slight deviations from perfect constancy being determined with great exactness by a Lord Rayleigh barometer.

The receptacle for containing the gas consisted of two parts, — a large bulb A for holding the total volume of the gas at 0°, and a supplementary bulb (between a and b) for accommodating the increase of volume at 32.383°. These volumes were made as nearly as possible 0.273 liter and 0.0324 liter, proportional to the absolute temperatures used; and each was fixed by a mercury meniscus set by making exact electrical contact with a very finely pointed stout platinum wire firmly fused into the glass.

The bulbs were surrounded by a large vessel, in which were placed in succession the two substances, ice and sodic sulphate, used to fix exactly the lower and upper temperatures.

The framework which supported this vessel or bath was made of stout, well-seasoned pine scantling, mortised and diagonally braced so as to offer great rigidity in all directions. The purpose of this bracing was to prevent any change in the relative heights of the platinum points in the bulb and the side tube. This support was held in place on the floor by four heavy bolts set in cement and imbedded in the ground under the concrete. A bar of two-centimeter channel-iron, similarly bolted down, was forged into the form of a large inverted U extended up and over the middle of the bath support, with which, however, it was not allowed to come in contact. To this bar were firmly wired and cemented with marine glue the tube from the top of the bulb and the upper end of the side tube. Thus the fixed position of the bulb was secured by two supports independent of the building and of each other, — at the bottom by the frame of the bath, and at the top by connection with the iron rod. Both supports were unaffected by temperature changes, because of constancy in the temperature of the room. The frame of the Lord Rayleigh barometer was likewise independently bolted into position.

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* Regaud and Fouillard, Z. wiss. Mikroscop., **20**, 138 (1903); also Journ. Anat. et Phys., **36**, 574 (1900).

The top of the wooden support around the bath was completely covered with a large plate of glass, through a hole in the middle of which rose the upper edge of the bath itself. The joint between the two was filled with marine glue. The cover of the bath was of felt incased in black enamel cloth. By having everything at the mouth of the bath thus capable of being washed, the chance for the introduction of impurities was reduced to a minimum.

A bulb made as nearly as possible like the one used in the preliminary experiments was again employed, and no essential change was made in its arrangement. The lower end of the bulb tube, however, to which the rubber tube leading to the mercury levelling reservoir V had formerly been directly attached, was made to dip into a cup completely filled with mercury and closed at the top by a rubber stopper cemented over with marine glue. This cup, not shown in the diagram, was provided with a side tube near the top to which the rubber tube was attached. This arrangement served as a trap to catch any possible sulphide of mercury formed by the action of the mercury and the rubber and to prevent its passage into the bulb.

In the Lord Rayleigh barometer, which determined the constancy of the pressure throughout the experiment, the position of coincidence of the mercury surface with the lower point (1) of the iron rod (F) was now found by the making of electrical contact instead of by observation through a small lens as before. This electrical method was made possible by cutting the iron rod in two parts and by slipping a very thin sheet of mica for insulation between them. The parts were firmly fastened together again by a collar made of a closely fitting glass tube held in sealing-wax. This change is not indicated in the diagram. The lower end of the iron rod was provided with a sharp platinum tip, which allowed greater accuracy in setting.

In order to read accurately the position of the upper meniscus with respect to the upper iron point, a background, black above and white below, was always adjusted so that the dividing line between the black and white surfaces was exactly tangent to the mercury meniscus, as viewed by the carefully levelled telescope. In this way an exceedingly sharp definition and reading may be obtained, as is well known. Inadequate precautions concerning this point undoubtedly vitiated to some extent the preliminary determinations, but the readings obtained in the determinations discussed below are believed to have been very exact.

A few preliminary trials with the new apparatus under its improved conditions served to show that the accuracy of the determinations of the pressure of the gas, as observed by means of the Lord Rayleigh barometer, had been increased nearly tenfold. Since this measurement now overstepped in accuracy all the others involved in the experiment, it became necessary to improve all the others to an equal degree of precision.

It is obvious that of the three variables — volume, pressure, and temperature — temperature alone requires reference to some generally accepted standard in order that the results of this investigation may be compared with those previously obtained and in order that they may readily be made use of in other calculations. Since changes in volume and pressure are purely relative, the use of the same standards throughout is all that is required; but for the sake of convenience and consistency the international standards were used throughout.

THE MEASUREMENTS OF VOLUME.

A volume is most conveniently measured by weighing the water or mercury which fills it, and making the appropriate corrections for temperature and pressure. For this reason the standard of volume, the liter, is fixed as the space occupied by a kilogram of water at 4° corrected for the weight of the displaced air, but not for the contraction of 0.000043 produced by the pressure of the atmosphere. This standard is used throughout the present work.

It becomes now a matter of importance to decide upon the liquid to be used in the actual measurement of the volume. Into this decision several factors enter.

In the first place, the internal and external pressures upon the rather thin large bulb must be during the measurement as nearly as possible those under which it is actually used. For this reason mercury was rejected as the standard liquid in this case, because its weight would inevitably distort the bulb. Another objection to the use of mercury is the fact that in order thoroughly to expel the air when a large bulb is being filled, the mercury must be boiled in the bulb. This involves the heating of the bulb to a high temperature, — an operation inevitably causing an increase of volume which only slowly readjusts itself, as in a thermometer thus heated. Regnault continually adopted this practice, but it cannot but be considered as dangerous when great accuracy is desired. These objections are less applicable to the use of mercury in the case of the smaller supplementary bulb, for this was so stout as to be scarcely susceptible of deformation by the slight pressure of the small column of mercury which it contained, and could easily be freed from air by exhaustion.

In the next place, the conditions of measurement also must as nearly as possible approach those of the actual expansion-experiment. Especially, because the gas volume is always in contact with mercury, the meniscus used to determine the volume must in each case assume the same shape, and therefore be measured at the same temperature and be set in the same fashion. This condition decides that mercury must be used in measuring the volume of the supplementary bulb, and demands that the temperature at the upper setting should be zero, and that at the lower setting 32.38°, the actual temperatures used in the final experiments. Fortunately, because the volumes of mercury are small, this demand is not inconsistent with adequate accuracy as to the other attendant conditions.

One other point proved to be at least equally important; namely, the increase of volume of the large bulb upon warming from 0° to 32.38°. This increase, of course, adds to the volume of the auxiliary bulb, constituting the total gain in volume with change of temperature. Two alternatives were open, — either the coefficient of expansion of the glass could be calculated from the weight of water filling the bulb at 32.38°, or else the linear coefficient of expansion might be measured directly.

After a number of time-consuming preliminary experiments it was decided to adopt the latter course, because the expansion of water over the range in question is six times as great as that of glass, and hence any error in the assumed value of the former or in our measurements would cause a sixfold percentage error in the coefficient of expansion sought.

In view of these considerations, the following means of measurement were adopted: The bulb and supplementary bulb were cut off from the rest of the apparatus somewhat below the lower pointed platinum wire (b), and a glass stopcock was attached at the junction. The total volume between the stopcocks was now found by weighing the bulb full of water at 0°; the volume from the lower stopcock to the upper contact point (a) was found by weighing the mercury which filled this at 0°, and the volume between the lower stopcock and the lower point (b) was found by weighing the mercury which filled this at a higher temperature. The linear coefficient of expansion of the glass was then determined with great care.

From these data the volumes sought may be calculated with as great accuracy as is possible under the circumstances. The details of the measurements are given below.

The bulb, filled with air dried by passage over potassic hydroxide, was balanced against a sealed counterpoise of approximately the same volume. Observations of temperature and atmospheric pressure necessary for the calculation of the weight of air contained in the bulb were also made. The weight of water of the corresponding volume at 0° C. was next obtained as follows: A levelling bulb was connected with the temporary stopcock at the lower end of the bulb by a rubber tube. Through this the bulb was filled with pure water to the upper stopcock. The lower stopcock was then closed and, in order to remove the dissolved air, the water was boiled in vacuo in the bulb. After the amount of water had again been adjusted by opening the lower stopcock so that it filled the bulb to the upper cock, this latter cock was closed and all was packed in ice for one and a half hours. In a special experiment this time had been found amply long enough for the required degree of accuracy in temperature. The lower stopcock was then closed (the upper one still remaining open), the bulb and projecting tube were cleaned and dried, and the levelling bulb was removed. When the same temperature as that within the balance case had been obtained, the bulb and water were weighed and the volume from stopcock to stopcock was calculated.

These weighings of the bulb filled with water indicated 391.900, 391.904, and 391.903 grams; average, 391.902 grams. The weight of the bulb filled with pure dry air under the same conditions of temperature and pressure (20° and 752.9 mm.) was 85.192, and the air which it contained must have weighed 0.366 gram. Therefore the water which it contained must have weighed 391.902 + 0.367 – 85.192 = 307.077 grams. If the density of water at 0° is taken as 0.999868 *, the total volume of the bulbs is found to be 307.118 milliliters ± 0.001. This measurement was made when the bulb was full of water, but in other respects under exactly the same conditions of temperature and pressure as in an actual gas measurement. The average pressure of the column of water inside during the measurement of volume was less than 8 millimeters

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* Chappuis, Trav. et Mém. du Bureau des Poids et Mes., **13** (1904).

of mercury, a pressure which would produce an increase of volume in the globe of less than 0.001 milliliter,* hence this distention during measurement may be neglected. If mercury had been used instead of water it would have been a very serious possible cause of error.

In order to obtain actually the volume occupied by the gas at 0° the volume below the upper platinum point must be determined and subtracted from 307.118. Therefore mercury was next run into the bulb from below to the upper platinum point, the air bubbles were removed by exhaustion, and after equilibrium of temperature had been reached in the ice bath, the exact adjustment of the mercury to the level of the platinum point was accomplished by a fine screw and indicated by electrical contact. The stopcock was then closed, the rubber tube removed as before, and the mercury inclosed in the bulb run out and weighed. Three successive experiments gave 472.21, 472.14, and 472.19 grams; in average, 472.18 grams. If mercury has a density of 13.5956 at 0°, this volume is then 34.730 milliliters ± 0.001. The mercury was so shallow and this bulb so stout, that it could not have been appreciably distended during measurement. The actual volume occupied by the gas at 0° must therefore have been $307.118 - 34.730 = 272.388$ milliliters, ± 0.002.

To ascertain the total volume of the supplementary bulb and the large bulb taken together, — namely, the volume from the upper stopcock to the lower platinum point, — the small volume between the lower stopcock and the *lower* platinum point was found and subtracted from the total volume 307.118. Instead of measuring this small volume at 0° C., it was done at a higher temperature, in order that the shape of the meniscus at this point might be more nearly that which it assumed during the performance of the main experiment.† After dividing by the density of mercury and making correction for the contraction of the glass, the volume at 0° was found to be in five determinations, — 1.944, 1.941, 1.946, 1.944, 1.943; average, 1.944 ± 0.0008 milliliters.

Thus the volume of the large bulb and the supplementary bulb together at 0° was 307.118 — 1.944 = 305.174 milliliters. This volume was sought at 32.38°, however, not at 0°, therefore the coefficient of expansion of the glass must be determined and the appropriate correction applied. It is easily calculated that the slight difference between the expansion of the projecting platinum points and the glass is wholly negligible, causing a possible error in the volume of only about 0.00002 milliliter. Therefore the coefficient of expansion of glass alone need be considered.

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* Lord Rayleigh found in a 2 liter globe a distention of 0.6 milliliters, and Cooke and Richards found in a 5 liter globe a distention of 1.7 milliliters for each atmosphere of internal pressure. Our bulb was at least as stout in proportion as these, hence the above conclusion.

† This determination should have been made at 32.4°. It was, as a matter of fact, through some oversight, made at 18.3°, where the average amount of mercury found was 26.350 grams. The breaking of the tube made a redetermination at 32.4° impossible, but the above value can hardly be essentially wrong.

For the sake of simplicity of manipulation the measurement of the coefficient of expansion of glass was made upon the side tube which had been cut off as already explained. The assumption here made that the glass of the bulb and of the side tube was of the same quality seemed admissible both because of the homogeneous appearance of the glass itself at the line of welding and because of the consideration that such a union could be made only between pieces of glass of approximately the same coefficient of expansion.

After a cross had been scratched with a diamond a few centimeters from each end, the tube was mounted on a firm support the height of which could be regulated by a finely threaded screw. Connections were made so that a rapid stream of water from a large reservoir could circulate through the tube and a thermometer for reading the temperature of this water was inserted into the middle of the tube. The tube as well as the connection to the reservoir were wrapped in cotton-wool except for the spaces about the crosses and the position opposite the thermometer scale.

The reservoir was now filled with ice and water, and after the temperature of the stream of water had come to equilibrium, the lower cross on the tube was adjusted by means of the fine screw of the support to the same level as the cross-hair in the eyepiece of the cathetometer telescope. The position of this cross-hair was kept fixed throughout the experiment, and was made the permanent point from which changes in height were measured. The position of coincidence of the cross-hair of a second telescope with the image of the upper cross on the tube was read off on the dial of the micrometer which bore this cross-hair. When this position had been determined by the average of several settings, the tube was readjusted in respect to the lower cross and the height of the upper cross was again read. This performance was repeated several times until the tube until the exact distance between the upper cross and the lower cross was well established.

Warm water was then substituted for the ice-water and a similar set of adjustments were made. Thus, since the lower cross was always set at the height of the permanent cross-hair in the lower telescope, the whole expansion of the tube was observed by the movement of the micrometer which bore the cross-hair in the upper telescope. The temperature of the stream of water was noted at the time of reading, and also the temperature of the cathetometer was taken in order to correct for the thermal expansion of this instrument, in case there had been a slight change.

The total distances between the two crosses was determined by direct reference through the telescopes to the brass meter stick to be 611.3 mm. In the telescopes a magnification was used greater than the standard adopted for all other determinations. It was necessary therefore to refer the micrometer dial to the brass meter stick. One dial division was found to equal 0.0886 mm.

Two series of determinations of the expansion of the tube were made — the first in the manner described above; but in the second the cotton-wool insulation was replaced by a glass jacket which was filled successively with melting ice and with warm water. In this determination the temperature of the tube was taken as the average of that of the stream within and of the water of the jacket without. The two were of course very near together. The latter measurements are rather the more satisfactory, because the temperature was more certain.

EXPANSION OF GLASS.

	Expansion of Tube (Corrected).	Change in Temperature of Tube.	Linear Coefficient of Expansion of Glass.
	mm.	° C.	
I.	0.186	36.0	0.00000846
	0.182	35.9	0.00000832
	0.183	35.9	0.00000836
III.	0.185	35.9	0.00000844
	0.182	35.9	0.00000832
Average coefficient of linear expansion .			0.00000838 ± 0.00000002
Coefficient of cubical expansion			= 0.00002524 ± 0.00000006

This is very near the average value 0.000025 found by others with soft glass of this kind. Therefore the volume of the two bulbs together at 32.38° becomes

$$305.174\ (1 + 0.0000252\,t^{\circ}) =$$
$$305.174\ (1 + 0.000817) = 305.423 \text{ milliliters.}$$

It is well known that glass when heated assumes an increase of volume which is not at once given up on cooling. Thus the zero point of a thermometer made of hard French glass is lowered for a time by 0.03° after heating to 33°.* This corresponds to an increase of volume of only one in two hundred thousand, and is therefore on the limit of the accuracy of the above volume. Error from this source, slight as it might be, was partly if not wholly eliminated by determining the volume under conditions as nearly as possible like those used in the actual expansion experiments. The small temperature interval of 32.4° used in the present experiments is a very favorable circumstance, as regards this correction, because the error increases greatly with rising temperature. In a research aiming at greater precision than the present one, the point should receive careful consideration.

Measurements of Temperature.

The necessity of recording the temperature of the bath in units of the international standard has already been pointed out. The temperature of melting ice under atmospheric pressure is one of the bases of this standard, and the position on it of the transition temperature of sodic sulphate has been accurately determined by Richards and Wells as 32.383° on the hydrogen scale.† The temperature of the gas becomes, then, a question of the purity of the substances used in the bath.

The bath was filled with very clear pure washed commercial ice and distilled water. After standing half an hour the water was replaced with freshly distilled water which had been cooled to nearly 0° C. in Jena glass. By this means very little impurity from melting ice was introduced. As a matter of fact, careful comparison of the melting point of this ice thus measured was found to be within a thousandth of a degree of that of the purest ice made from boiled distilled water, wholly in platinum. Moreover, the higher temperature was read in such a way as to eliminate any error from this source, so that the results cannot be affected by any impurity in the ice.

Because ten kilograms of sodic sulphate was needed to keep the bath at 32.38°, the preparation of the salt in a perfectly pure state was a serious task. Therefore, instead of always using sodic sulphate of the greatest possible purity, only moderate precautions were used, and the presence of slight impurities was corrected for by observing the temperature of the melting mass on the standardized Baudin thermometer number 9390. A very small amount of impurity did not affect the constancy of the point, but only its absolute position. The zero point of this thermometer was determined immediately afterwards in each case by plunging it into ice, which had been prepared similarly to that for the bath itself; thus was the actual interval over which the gas had been heated recorded on the thermometer.

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* Notice sur les Thermom. à mercur. Bureau Internat. Poids et Mes. (1896), p. 9.

† Proc. Amer. Acad., **38**, 431 (1902).

In order to determine the exact value of the temperature interval thus found on the international scale, the thermometer was afterwards standardized by reading it in the purest sodic sulphate many times recrystallized and then in purest ice. The following changes in temperature were observed: 32.580 — 0.103 = 32.477; 32.583 — 0.107 = 32.476; 32.579 — 0.101 = 32.478; average, 32.477.

Because in these tests exactly as much of the thermometer was exposed to air at 20° as in the actual measurement, the reading 32.477 signified the transition temperature of pure sodic sulphate, a temperature of 32.383°. In order to obtain the true temperature, 0.094° must be subtracted from the reading of the thermometer. This was done in each case.

In a few cases the temperature is recorded as 32.384°, or 0.001°, above the maximum temperature given by the purest sodic sulphate. This difference was probably due to a slight error in thermometry; but since it may have represented the real interval, — the excess being due to a trace of impurity in the ice, — the reading is recorded as found.

Measurements of Pressure.

The standard of length, in terms of which pressure was measured, was kindly furnished us in terms of the international meter by the National Bureau of Standards in Washington, by their calibration of our Geneva brass meter-bar with silvered scale, at 20.5° C. The scale was found to be amply accurate enough for our purpose, no single centimeter varying more than 3 microns from the mean, and very few varying more than 1 micron. No length of 20 centimeters on the scale varied from the average value by more than 0.01 millimeter. The actual readings, however, were recorded in terms of the dial divisions of the micrometer screw which carried the cross-hair in the eyepiece of the telescope.

The evaluation of these divisions was made by repeatedly noting the number of divisions passed through in changing the setting of the cross-hair from coincidence with one mark of the meter-bar to coincidence with another. It was found that the distance from the telescope to the object observed must not vary more than half of one millimeter in order to preserve this value to the required accuracy. The distance from the upper iron point of the Lord Rayleigh barometer to the object lens of the telescope — 775.0 mm. as given by concordant measurements — was adopted as standard whenever the telescope was used. The following table contains the comparisons of dial divisions with the length of separate successive lengths of two millimeters each. The measurements were made from two independent adjustments of the focus, with very careful measurement of the distance between the meter-bar and the telescope. Each of these figures represents the mean of these measurements.

Designation of Distance Measured.	Value in Micrometer-Dial Divisions.
31.0–31.2	162.2
31.2–31.4	162.7
31.4–31.6	162.0
31.6–31.8	162.5
31.8–32.0	162.1
32.0–32.2	162.0
32.2–32.4	162.7
32.4–32.6	162.6
32.6–32.8	162.7
32.8–33.0	162.1
31.4–31.6	162.1
Average, 2 mm. of scale . .	162.34 ± .06

The slight differences between these measurements are due in part to necessary experimental error, and in part to the slight inaccuracies of the divisions measured; but the probable error of the average is so small as to be negligible. According to the report of the National Bureau of Standards, a millimeter in this part of the scale has the average value of 1.0004; hence a single dial division has the value in millimeters of $\frac{2.0008}{162.34} = 0.012325 \pm 0.000005$. This value was used throughout the work.

Before proceeding to the measurement of the pressures exerted by the gas during the experiment, that constant correction due to the difference in the distance apart of the platinum points in the bulb and in the side tube was evaluated. As in the preliminary experiments, the bulb was placed at the arbitrary standard distance from the telescope and the difference in level of the upper pair of points was observed by successive settings of the cross-hair of the telescope upon each point. The telescope was then lowered and a similar set of observations of the lower points was made. Then the position of the upper points was again determined. This first series showed the points in the bulb to be higher than those in the side tube — for the upper pair by 0.749 mm., 0.750 mm., 0.752 mm.; 0.751 mm., average 0.751; and for the lower pair by 0.167 mm., 0.169 mm., average 0.168 mm.

These showed as the average the distance apart of the points in the bulb to be 0.583 mm. greater than the corresponding distance in the side tube.

The second series of measurements was made after the bulb had been readjusted in respect to its distance from the telescope. The further precaution was also taken of viewing the points from the opposite side of the bulb in order to eliminate any error due to possible irregular refraction of the glass.

In the second series, the heights of the bulb points exceeded those of the side points, in the case of the upper pair by 0.753 mm., 0.754 mm., 0.752 mm., average 0.753; and in the case of the lower pair by 0.167 mm., 0.169 mm., 0.170 mm., average 0.169.

These gave the average greater distance apart of the bulb points as 0.584 mm. (agreeing as nearly as is reasonable with the proceeding), and so for the total average of all determinations 0.5835. These measurements were made at 20°, while the tube was used at 0° and 32.4°, but the effect of the corresponding dilation is negligible. The difference of mercury level at 32.4° must nevertheless be reduced to 20° (at which the main barometer was read), before it is added to the reading of the main barometer. The value then becomes 0.582, which is used as K in the calculation on page 135.

Although the *change* in pressure of the gas with change in temperature must be determined with the utmost accuracy, the actual pressure which the gas exerts need be known only approximately. An inspection of the formula for calculation on p. 135, where this value P enters both the numerator and the denominator, makes this fact obvious. An accuracy to within half a millimeter was shown by calculation to be quite sufficient. Since the pressure of the gas is measured on the Lord Rayleigh barometer by the height of the mercury meniscus (m) above the lower point (1), and since the distance from the meniscus to the upper point (n) is determined during the course of the experiment, it only remains to find the distance between the two points. In making this measurement, the cross-hair of the telescope was set upon one of the points in question. The telescope standard was then revolved so that on a vertical axis this height could be directly read on the silvered brass meter-bar, which had been placed at the proper distance from the object glass. The height of the other point was determined similarly. Two determinations, giving 761.33 and 761.35 when corrected to the international meter, agreed in showing the distance between these points to be 761.34 mm. This measurement, like all the other measurements concerning the pressure, was made at 20°.

The actual pressure of the gas in the tubes leading to the bulb was of course indicated by the barometric column thus read, plus the very small pressure (usually 0.03 mm.) of the residual gas in the Torricellian vacuum. This latter was kept as constant as possible by a good Sprengel pump, and read from time to time with a McLeod gauge.

The McLeod gauge was so made that a difference of pressure read in the fine tube was one hundred times as great as the real pressure being determined. It was only necessary, therefore, to read this gauge to an accuracy of 0.1 mm. Since, moreover, the only requisite is that this pressure shall remain about constant within a small known range throughout the course of an experiment, a possible inaccuracy in registration of the gauge due to adsorption * would make no difference, applying alike to all measurements, and cancelling from the final result.

The manner of making the pressure readings was the same as that previously used, except for the improvement in the background already described. The following typical day's record shows the constancy of reading attained and the usual magnitude of the corrections which were applied.

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* Ramsay and Baly, Phil. Mag. [5], **38**, 314 (1894).

February 28, 1902. Ice in Bath at 12.30 p.m. Pure previously Boiled Freezing Water run in in Place of Ice-Water at 2.00 p.m. Meniscus above the Point.

		Successive Readings.				
		1	2	3	4	5
Hour	. . . . .	2.15	2.40	3.05	3.50	4.20
Temperature of barometer	°C (upper) °C (lower)	20.0 20.0	20.0 20.0	20.0 20.0	20.0 19.9	20.0 20.0
McLeod gauge with corresponding pressures . .	dial divisions millimeters	329 0.041	308 0.038	267 0.033	256 0.032	250 0.031
Reading of cross-hair set on meniscus	dial number	32.6 32.6 32.5	48.4 48.3 48.5	38.7 38.9 38.9	44.3 44.1 44.5	4.0 3.8 4.0
Revolutions of dial* . .	. . . . .	2	2	2	2	2
Reading of cross-hair set on point	dial number	35.4 35.6 35.6	0.9 1.2 1.2	42.3 42.5 42.7	47.5 47.8 47.5	7.7 7.7 7.8
Distance between meniscus and point	dial divisions millimeters	103.0 1.269	102.5 1.263	103.7 1.278	103.3 1.273	103.8 1.279
Corrected excess of pressure of gas over height of iron rod	millimeters	1.310	1.301	1.311	1.305	1.310
Average		1.307 ± 0.001 mm.				

Because the iron rod was 761.34 mm. long, the total height of mercury at 20° supported by the gas pressure was 762.647 millimeters. The points *a* and a^1 being essentially on the same level, this is also essentially the pressure of the gas in the bulb. Each determination of the coefficient of expansion yielded a corresponding table at 0°, and another similar one at 32.48°. The difference between the corrected values for the two temperatures is recorded in the tables on pp. 136, 139 as *p*.

A change in atmospheric pressure affects equally the levels of the mercury in the lower and in the upper part of the Lord Rayleigh barometer. Provided, however, that the pressure on the lower meniscus, fixed by the pressure in the side tube of the bulb, did not alter, a readjustment of the lower level into contact with the lower point (1) of the barometer would bring the upper level also back to its proper place. In practice the reading of the upper mercury level was taken within a minute after the adjustment was made. Under ordinary atmospheric conditions, no barometric change sufficient to invalidate the setting takes place in so short a time. Thus atmospheric changes could be neglected, unless the atmospheric barometer was changing with unusual rapidity, in which case measurements had to be suspended.

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* One revolution of the dial equals fifty dial divisions.

The temperature correction of the Lord Rayleigh barometer is based on the difference between the change in length of the mercury column, due to change in the density of the mercury, and the change in the length of the iron rod. This amounts to 0.136 mm. per degree centigrade, which is to be subtracted from the height of the mercury meniscus when the temperature of the barometer is above the standard (20° C.). The temperature of the barometer was taken as the mean of that recorded by a standardized thermometer at the bottom and another at the top. In most cases no correction at all was applied, because the room was kept at constant temperature and the air in it was thoroughly stirred by a large electric fan. Nevertheless it is probable that slight fluctuations of a few hundredths of a degree often occurred, and it would have been better to surround the iron stem with a very accurate constant temperature bath. The accuracy was increased by taking many observations over several hours, the average of which would of course be more precise than a single setting, because it would represent an average temperature; but it is probable that this point was the weakest one in the present series of measurements, and accounts for the most of the variations in the preceding table as well as for those in the final tables of results. This conclusion is based upon the evidence found in the foregoing table that the agreement between successive readings of pressure at a given time was closer than between the averages at different times. These differences could hardly be due to the electrical contact arrangement, since the levelling bulbs were adjusted by means of very finely threaded screws and the current used to show the contact was of too low strength and too small voltage to allow perceptible sparking. Moreover, the tubes were so wide and the platinum points were so sharp that no difference in position was noted between the making and breaking of contact. It may be noted that the variation between the readings, undesirably large as it is, does not exceed that observed by Chappuis in his admirable work on the constant-volume hydrogen thermometer. The measurement of pressure more accurately than this is an exceedingly difficult problem.

In preparing the bulb for the introduction of the gas, it is of great importance to remove as far as possible all other adsorbed gases, of which water vapor probably forms the most dangerous component. After dry air had been passed through the bulb for several hours, it was exhausted by means of a Sprengel pump and the outside was heated with hot water to about 70° C. Dry gas was next admitted, and then the bulb was again exhausted. This process was repeated three times, after which dry gas was allowed to stream through the bulb from two to three hours. The mercury used in the bulb was dried by heating it to 150° C., and dry air was drawn through the rubber tube which connected the lower part of the bulb with the levelling bulb for five hours.

Calculation of Results.

The value sought in the work is the coefficient of expansion of each gas under constant pressure; but because it was impracticable to keep the pressure absolutely constant a slight correction had to be applied for changes. The consideration below shows that Boyle's law may safely be used in referring these changes to changing volume. The actual variation of pressure in the case of hydrogen was about 2.5 mm., and Regnault found that for this gas the product of pressure and volume varied from constancy by less than one part in two thousand for an increase of an atmosphere in pressure. This correction would amount, then, to an error in volume of not over 0.0005 c.c. for a change of $\frac{1}{300}$ atmosphere in these experiments, a quantity which is beyond their limit of accuracy. Hence, for this very small range of pressure Boyle's law may be used as exact.

Accordingly, in the previous paper, the equation used for calculating the results was as follows:

$$a = \frac{(P + p - K)\,(V + v) - PV}{PVt}$$

in which a equals the expansion per degree Centigrade of unit volume at 0° C.; V equals the volume at 0° C.; v, the increase in volume; t, the difference in temperature between the two baths; P, the original pressure at 0°; p, the small increase of pressure in the gauge on the reading at the higher temperature; and K, the constant value to be subtracted from p due to the greater distance apart of the platinum points in the side tube over the distance apart of those in the bulb.

In this equation no account is taken of the fact that the mercury enclosing the gas has a higher vapor tension at 32.4° than at 0°. This correction was then omitted because it was distinctly beyond the probable accuracy of the work. In the present case, however, the vapor tension of mercury at 32.4° (about 0.003 mm., according to Morley)* must be considered, because it is larger than the probable error of the pressure readings. The pressure at 0° is undoubtedly less than 0.001 mm. and therefore negligible even here. It is of course not quite certain that the gas is wholly saturated with mercury vapor, but since several hours were allowed to pass before the final readings were taken, the saturation was probably almost complete. The equation giving the desired result is therefore

$$\alpha_p = \frac{(P + p - K - 0.003)\ (V + v) - P V}{P V t}$$

Here $V = 0.272388$ liter, $V + v = 0.305423$ liter, and $K = -0.582$ mm., as recounted in the preceding pages. The other quantities in the equation are given below for each experiment.

THE COEFFICIENT OF EXPANSION OF HYDROGEN.

Hydrogen was made electrolytically from pure hydrochloric acid, using a platinized platinum cathode and a zinc amalgam anode. It was purified by passage over platinized asbestos, through two tall drying towers filled with solid potash sticks and over phosphoric oxide. The hydrogen entered the bulb from the top, and "dead ends" were avoided as much as possible in the supply system. The method of enclosing within the bulb an amount of gas suitable for the experiment was not modified from that used in the preliminary work.

In the following table are contained the eight last consecutive and most satisfactory determinations made with pure hydrogen gas. Numbers 1–5 inclusive are measurements on the same hydrogen, and numbers 6–8 inclusive are determinations made after a complete repetition of the process of drying and filling the bulb.

The "probable error" of these results, computed according to the method of least squares, is ±0.00000003. This does not mean, however, that the expansion of hydrogen is known to an accuracy of three in the sixth significant figure, because at least one quantity entered into the calculation of this coefficient which has a possible error of one in the fifth significant figure; but it does show that accidental errors of reading tem-

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* Morley, Phil. Mag. (1904), June, 663.

HYDROGEN.

No.	P.	p.	t°.	α_p.
	mm.	mm.	°C.	
1	762.6	–2.438	32.384	0.0036607
2	"	–2.437	32.384	0.0036608
3	"	–2.437	32.384	0.0036609
4	"	–2.437	32.382	0.0036610
5	"	–2.437	32.382	0.0036610
6	762.4	–2.440	32.382	0.0036608
7	"	–2.443	32.378	0.0036611
8	"	–2.443	32.378	0.0036611
		Average		= 0.00366092

perature and pressure and errors of manipulation arising during the performance of the experiment have a "probable error" of only one in a hundred thousand. It seems plain, therefore, that farther advance in accuracy can be attained only by improvements in the methods of measuring volumes and the expansion of the various solid and liquid substances connected therewith, and in the measurement of temperature. These difficulties must enter equally into any other investigation with the same object. When these are improved, the method will give yet better results.

The difference between the final result, 0.0036609, and that found in the preliminary work, 0.003659, is no greater than the known experimental error of the preliminary work, which made no pretensions to absolute accuracy, but was intended only to outline the capabilities of a new arrangement of apparatus.

The comparison of this result with the work of others is much complicated by the fact that no one else has worked under similar conditions. Nearly every one has chosen a wider range of temperature, namely, from 0° to 100°; and, moreover, very few have worked upon the volume-increase, but have chosen rather the pressure-increase in constant volume.

The old result of Regnault,* 0.0036613, is indeed not very far from the new one, but has too large a possibility of error to afford important evidence. More recently, the coefficient of expansion at constant pressure has been studied very carefully by Chappuis,† who finds that the volume-change per degree under constant pressure is 0.0036600, a value noticeably lower than ours. The pressure was, however, different from ours, and the range of temperature greater.

The value corresponding to tension-increase in constant volume has been found by three separate experimenters recently to be about 0.00366256,‡ as follows:

Chappuis	0.00366256
Travers	0.00366255
Onnes	0.00366257
	0.00366256

There can be no doubt that the value for constant pressure is less than this, because $p\,v$ with hydrogen undoubtedly increases as the volume diminishes. According to Regnault, if $p\,v$ at a pressure of one meter of mercury is taken as 1.00000, that at 2 meters is 1.00043, that at 4 meters is 1.00153, and that at 8 meters is 1.00424. By plotting these figures as ordinates and the pressures as abscissae, there is obtained, as is well known, a curve which is almost linear, and is therefore capable of accurate use in graphic calculation. The application of this curve to the present case is now to be discussed.

Imagine a mass of gas at the temperature 32.38° under atmospheric pressure compressed further until it assumes the volume occupied by the same mass of gas at 0° and atmospheric pressure. Its tension will now be 1.12 atmospheres. For this increased tension, by a slight extrapolation of Regnault's curve, it is easy to find that the value for $p\,v$ would be about 1.000044§ or $\frac{0.0044}{0.12} = 0.037$ per cent of the increase in pressure. Thus it would appear that the pressure-coefficient in constant volume should be about 0.037 per cent greater than the volume coefficient under

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[*] Regnault, Mémoires de l'Académie des Sciences, **21**, 116, 426 (1847).

[†] Chappuis, Rapports du Congrès International de Physique, **1**, 133 (1900). Trav. et Mém du Bur. Int. Poids et Mes., **13** (1903.) See also Travers, The Experimental Study of Gases, p. 149 (Macmillan, 1901).

[‡] Travers, Chem. News., **86**, 61 (1901 ?).

[§] Various graphic calculations gave figures varying from 1.000042 to 1.000046.

constant pressure, or the latter would be 0.00366256 — 0.00000134 = 0.0036612, a value but little above the value 0.00366092 found in the present series of experiments. An objection to this comparison lies in the fact that Regnault made his measurements of the change of $p v$ at 4°, and not at 32°; but probably this difference would not affect very seriously the results.

Lord Rayleigh, in his recent careful determination of the compressibility of hydrogen, has found that if the value of $p v$ at one atmosphere's pressure is taken as 1.00000, at half an atmosphere's pressure it will be 0.99974.* The results of Regnault given above show that this change is nearly linear with the pressure, hence the slight extrapolation giving the value 1.000062 for 1.12 atmospheres is permissible. Now $\frac{0.000062}{0.12}$ is 0.052 per cent, or the percentage difference between the coefficients of expansion in constant volume and that under constant pressure; therefore on the basis of the results of Travers and others just recorded, the latter value a_p should equal 0.00366065, while we find 0.0036609. The agreement is as good as could reasonably be expected, especially considering the fact that Lord Rayleigh's experiments were made at 11°, while ours demand results for 32°.

Thus if the usual value for the tension increase in constant volume is assumed as correct, the application of Regnault's value for the relation of pressure and volume would make our results appear slightly too low, while the application of Lord Rayleigh's value would make it appear slightly too high. While neither application is strictly precise, in any case it appears that the new value for the coefficient of expansion is not without support in other work, and may be not far from the truth.

Further work upon hydrogen seemed to be aimless unless much time was spent in the redetermination of the essential dimensions involved, — a colossal task, involving several separate investigations. Therefore another gas was studied.

THE COEFFICIENT OF EXPANSION OF CARBON DIOXIDE.

Carbon dioxide, made by the action of hydrochloric acid on marble and purified by passing through two wash bottles containing acid sodic carbonate solution, an Emmerling tower containing the same solution, two towers with sulphuric acid and over phosphoric oxide, gave the following results:

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* Phil. Trans., A **204**, 351 (1905).

CARBON DIOXIDE.

No.	P.	p.	$t°$.	α_p.
		mm.	°C.	
1	761.5	–0.983	32.376	0.0037277
2	"	–0.984	32.376	0.0037276
3	"	–0.974	32.376	0.0037282
4	"	–0.971	32.372	0.0037288
5	"	–0.971	32.372	0.0037288
			Average	0.0037282

The final value, it will be noticed, is in accord with that obtained in the preliminary work, 0.003727, having been increased by about the same small amount as has the figure for hydrogen. Except for the possibility of some error dependent on the nature of the gas itself, such as adsorption, the relative rates of expansion of hydrogen and carbon dioxide seem to be well established.

As has been suggested in the last paragraph, the value obtained from these experiments, as well as all those previously found by others, may contain a constant error of uncertain magnitude caused by the different amount of adsorption of the gas by the glass at the two different temperatures employed. In the case of hydrogen and glass this correction is probably small. A similar error would, of course, enter equally into the determinations of increased tension at constant volume, but the ratio of the results from the two methods might nevertheless be changed, since the constant volume measurements were made between 0° C and 100° C. Possibly the platinum-iridium bulb used by Chappuis may have exerted a slightly adsorbing action upon his hydrogen, and, in the case of carbon dioxide, the adsorption is probably of some importance. It is hoped that determinations of the actual amount of this correction will soon be made in this laboratory.

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SUMMARY.

Improvements in the surroundings, the stability, and the manipulation of the apparatus previously described for the determination of the coefficient of expansion of gases by heat under constant pressure are set forth. The possibility of measuring the pressure of a gas to an accuracy of one thousandth of a millimeter of mercury is shown, and some of the difficulties of the determination of volume and temperature to a corresponding degree of accuracy are pointed out.

Measurements of the coefficient of expansion of hydrogen (0.0036609) and of carbon dioxide (0.0037282) under constant pressure as far as five significant figures are recorded, and their probable reliability is discussed. The importance of knowledge of the amount of adsorption of gases by glass is mentioned in this connection. The results must not be considered as final measurements, but their consistency shows that the apparatus is capable of attaining a high degree of precision.